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**Polymerization**

# Visible-Light Hypervalent Iodide Carboxylate Photo(trifluoro)methylations and Controlled Radical Polymerization of Fluorinated Alkenes**

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Driven by the unique characteristics imparted by -CF$_3$ onto compounds from synthetic drugs to polymer nanostructures, trifluoromethylation (TFM) has recently become a very valuable technique for dramatically improving and expanding molecular properties and functions, and TFM chemistry has grown into an extremely active field.[1–13] While most TFM reactions involve nucleophilic[1–7] or electrophilic[1–5,8] organic or organometallic techniques,[1–6,9] radical TFM reactions[1–5,10–12] have emerged as a more convenient yet powerful strategy. However, while advances have been made,[10] metal-assisted CF$_3^{\bullet}$ generation from CF$_3$I ($b_p = -22.5\,°C$) and other sources[14] is expensive and inconvenient. Thus, increasing the availability of metal-free, safe, nongaseous, commercially available, inexpensive CF$_3^{\bullet}$ sources remains highly desirable.

Likewise, fluorinated (co)polymers are a fundamental class of specialty materials[15,16] requiring a precise synthesis. However, while controlled radical polymerizations (CRPs) have undergone remarkable developments for conventional monomers[17,18] they remain ineffective for highly reactive, main chain fluorinated monomers (FMs), such as vinylidene fluoride (VDF). Thus, because of the current lack of synthetic methods, the synthesis, characterization, and fundamental understanding of well-defined, complex macromolecular structures containing fluorine lag significantly behind those of conventional alkenes.[12–17] As metal-mediated alkyl halide initiation and CRP are not available,[19] FM-CRP is still accomplished at high temperatures and pressures with the oldest CRP method,[20] the iodine degenerative transfer[15–21] (IDT), using perfluorinated alkyl iodides (R$_F$-I)[21] as chain transfer agents (CTAs), and peroxide initiators.[15,16,20,21]

Consequently, FM-CRP development for the synthesis of elaborate architectures and characterizing the resulting fluoromaterials remain worthy endeavors.[15–22] Yet, such polymerizations are very challenging, as all FMs are gases ($b_p^{VDF}-83\,°C$). As such, reactions are typically carried out at $T \approx 100$–$200\,°C$, in expensive, high-pressure metal reactors[15,16,20,21] and studies of their kinetics involve many time-consuming, one-data-point, large-scale experiments. Thus, the development of mild temperature methods for low pressure, small-scale polymerizations in inexpensive glass tubes would be appropriate for rapid screening of catalysts and reaction conditions and also amenable to photochemistry.[19,23]

To address the problems above, we have recently reported[19] the first examples of metal-mediated controlled (CRP-IDT), and respectively free radical (FRP) VDF polymerizations, carried out at 40 °C, in low pressure glass tubes, using Mn$_2$(CO)$_{10}$[19] as a visible light photocatalyst, in conjunction with R$_F$Is and respectively alkyl halides, (including Mn$_2$(CO)$_{10}$ TFM with CF$_3$-I and CF$_3$-SO$_2$-Cl), as well as the complete activation of both -CH$_2$-CF$_2$-I and -CF$_2$-CH$_2$-I chain ends towards well-defined PVDF block copolymers.[19] Nonetheless, metal-free CRP methods also remain highly desirable.

Recently, hypervalent iodine(III,V) (HVI) derivatives have undergone a resurgence in organic chemistry,[24–26] and have become inexpensive, as illustrated by HVI carboxylates (HVICs) such as (CX$_3$COO)$_2$I$^{III}$Ph, (where X = H, ((diacetoxy)iodo)benzene, IDAB; where X = F, bis(trifluoroacetoxy)iodo)benzene, IFAB) and (CH$_3$COO)$_3$I$^{V}$(-C$_6$H$_4$COO-) (Dess–Martin periodinane, DMPI; Supporting Information, Figure S1). Although HVICs are predominantly used in oxidations,[24] alkyl radicals derived from their thermal- or UV-induced decarboxylation can add to alkenes or alkylate aromatics.[27] With I$_2$, HVICs mediate the hypoiodite reaction[24–28] of alcohols,[27–29] acids,[27] and amines[27] towards R-Y-I,[29–31] which photolyzes[32] to R-Y$^{\bullet}$ (Y = O, COO, NH). However, the potential of IDAB and IFAB as radical initiators[33] remains largely ignored,[34,35] and there are no reports on HVICs as well-defined CX$_3^{\bullet}$ or CX$_3$I sources or as initiators for FMs. Additionally, there are no reports on the use of IFAB as a TFM agent or on the photolysis of DMPI and its radical reactions.

As such, we suggest that for radical chemistry, room-temperature stable HVICs be considered protected synthetic equivalents of their expensive and hazardous[36] or inaccessible peroxide or azo derivatives. Thereby, R$_F^{\bullet}$ and CX$_3^{\bullet}$ become readily available through the metal-free, room-temperature, visible-light photodecarboxylation of the corresponding (RCOO)$_2$IPh HVICs.[24–26]

We are thus introducing IFAB, IDAB, and DMPI as the most practical and affordable green[37] CX$_3^{\bullet}$ and CX$_3$I (X = F, H) precursors, as exemplified by their use as visible light, FM-CRP photoinitiators and respectively, chain transfer agents. While the methods described herein are suitable for CX$_3^{\bullet}$ addition to other alkenes, in IDT-CRPs of other monomers, or in radical TFM of arenes, we have used this method with

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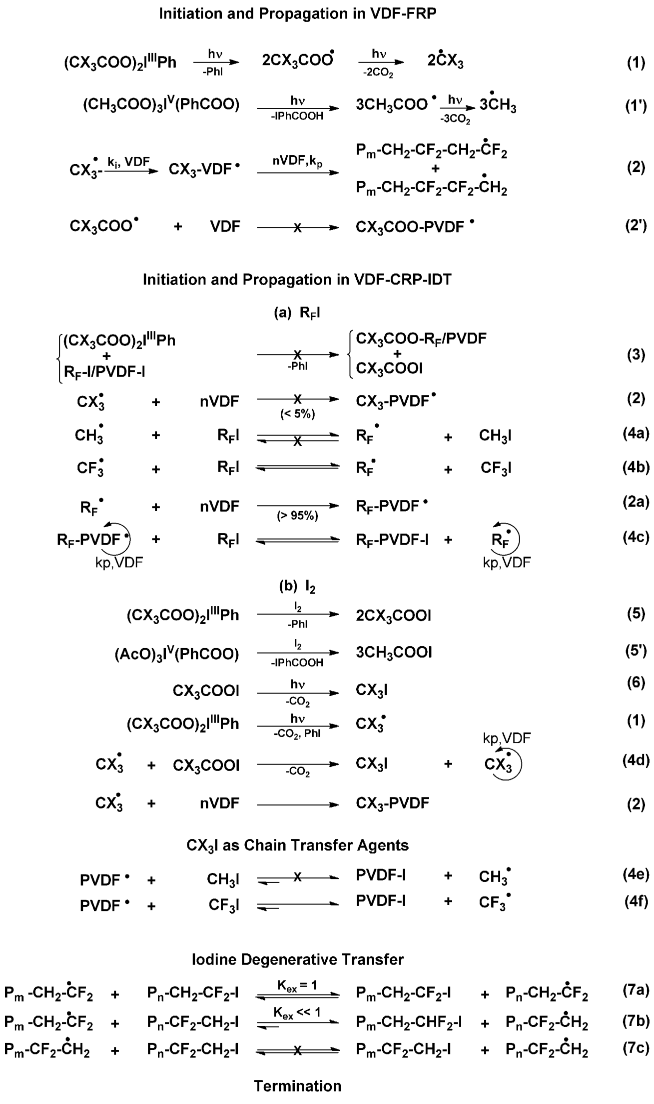
the more difficult VDF, in a metal-free IDT-CRP using $R_F$-I and $I_2$ chain transfer agents.

While thermolysis of IDAB at room temperature is negligible,[38] the room temperature UV photolysis of IDAB[38] and congeners[27] proceeds selectively to R$^•$ by way of diffusion-controlled decarboxylation.[27,39] It is thus expected that visible light photolysis of IDAB, IFAB, and DMPI is also homolytic (Table S1). To optimize the rate while maintaining safe pressure within the tubes,[19] we carried out all experiments at 40 °C (Figure S2), where out of the 28 solvents tested (Table S2), dimethyl carbonate was, once again,[19] found to be the best.

VDF polymerization begins with the photolysis of the weak[40] I–O bond. [Scheme 1, Eqs. (1) and (1′)].[24] Fast[27,39] $CX_3COO^•$ decarboxylation to $CX_3^•$ followed by VDF addition initiates polymerization, which propagates with both the 1,2- and 2,1-units [Eq. (2)].[19] $^1$H- and $^{19}$F NMR spectroscopy (Tables S1 and S3; Figure S3) confirm decarboxylation, $CX_3^•$ initiation, and the lack of IDT from unstable[24,34] iodanyl radicals (e.g. $CX_3COO$-I$^•$-Ph) or PhI, because of the lack of $CX_3COO$-PVDF [Eq. (2′)], the regiospecific[19] $CX_3$-$CH_2$-$CF_2$-PVDF addition, and the absence of PVDF-I chain ends. Kinetic experiments (Figures S3ef and S4; Table S4) revealed only free radical polymerizations, in which all HVICs gave similar efficiencies, and indicated that IDAB, IFAB, and DMPI are most likely difunctional and respectively, trifunctional initiators.



*Scheme 1.* Mechanism of the HVIC-photomediated VDF trifluoromethylation and IDT-CRP with external and in situ generated chain transfer agents (X = H, F).

Subsequently, we tried to establish HVIC-VDF controlled radical polymerizations. While $I_2$ was used[21] for acrylate and styrene IDT polymerizations in the dark,[41] FM-IDTs are still only[20] performed with expensive $R_F$-I chain transfer agents.[20,21] Nonetheless, potential HVIC reactions with $R_F$-I or $I_2$ (Scheme 1) should be considered. $CX_3COOI$ (quantitatively obtained from fast, dark, room-temperature reactions of $I_2$[24–32,42] or $R_{alk}$-I[43,44] with IDAB or IFAB) affects aromatic iodinations,[24–26] alkene iodoacetoxylations,[42] and may oxidize $R_{alk}I$ to $CX_3COOR_{alk}$.[43,44] However, while $R_{Alk,Ar}CH_2COOI$ hypoiodides are stable in the dark,[44] the weak O–I bond,[40] and strong COOI chromophore[44] enable efficient visible light photolysis,[29,30,42,44] where the R-independent rate-determining O-I homolysis, followed by fast decarboxylation[27,39] and $I_2$ trapping, provides $R_{alk}I$[27,28,32] within a solvent cage.[44] Consequently, RCOOIs mediate photohalodecarboxylative Hunsdieker-like HVIC reactions with R-I[43,45] or $I_2$,[24–28,32,44] which have not yet been used in TFMs or polymerizations.

While HVIC acetoxylation of $R_{alk}I$[43,45] may occur in the dark, UV photolysis of IDAB/$R_{alk}I$ proceeds with I atom

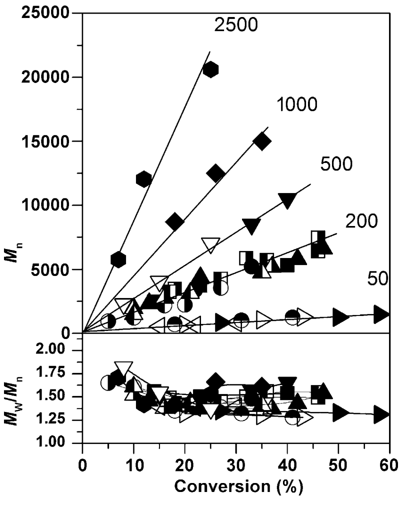


*Figure 1.* Dependence of $M_n$ and $M_w/M_n$ on conversion in VDF polymerizations initiated from IFAB, IDAB, and DMPI in the presence of $I(CF_2)_6I$. $M_n$ increases with conversion and [VDF]/[$I(CF_2)_6I$] ratio: [VDF]/[$I(CF_2)_6I$]/[IFAB] = 50/1/0.25 (▸); 200/1/0.25 (◨), 500/1/0.25 (▽), 500/1/1 (▼); 1000/1/1 (◆); 2500/1/1 (●). The same $M_n$ is obtained regardless of HVIC nature or amount: [VDF]/[$I(CF_2)_6I$]/[HVIC] = 200/1/[HVIC]: IFAB = 0.25 (◨), 0.5 (◧), 1 (■); IDAB = 0.25 (◑), 0.5 (◐) 1 (●); DMPI = 0.25 (◭), 0.5 (◮), 1 (▲). [VDF]/[$I(CF_2)_6I$]/[HVIC] = 50/1/0.1, IFAB (▷), IDAB (◓), DMPI (◁).

abstraction and $R_{alk}^{\bullet}$ generation.[28,43,45] Accordingly, control experiments confirm VDF-IDT controlled radical polymerization (Figure 1), PVDF-I iodine chain ends (Figure S5a,b), and the lack of $R_FI$ or PVDF-I acetoxylation (Table S1; Figure S5c). Thus, $CX_3^{\bullet}$ photogeneration [Eqs. (1) and (1′)] is much faster than esterification,[45] and perfluorinated alkyl iodides act solely as iodine chain transfer agents.[19,21] Kinetic $^1$H and $^{19}$F NMR experiments (Figures S5 and S6) revealed that, irrespective of conversion and consistent with the IDT mechanism,[15–21] less than 5 % of $CX_3^{\bullet}$ radicals add directly to VDF and more than 95 % of the chains are initiated by $R_F^{\bullet}$ [Eq. (2a)]. The continuous influx of $CX_3^{\bullet}$ radicals from the slow[38] HVIC photodecomposition serves mostly to abstract iodine from $R_F$-I, generating $R_F^{\bullet}$ and respectively $CF_3$-I, an excellent IDT mediator,[15,16,19–21] or $CH_3I$, a negligible[15,16,19–21] chain transfer agent (Scheme 1, [Eqs. (4a), (4b), (4e), and (4f)]; Table S1; Figure S3d) and to compensate for terminations.[46]

As such, I-$(CF_2)_6$-I is swiftly consumed[15,16,19–21] into macromolecular I-PVDF-I chain transfer agents [Eq. (4c)], which, through the thermodynamically neutral ($K_{equil}^{IDT} = 1$) IDT of dormant and propagating $P_m$-$CH_2$-$CF_2$-I and $P_n$-$CH_2$-$CF_2^{\bullet}$ [Eq. (7a)] enable VDF-IDT controlled radical polymerization.[15,16,19–21] Since $P_n$-$CH_2$-$CF_2$-I and $P_m$-$CF_2$-$CH_2$-I have vastly different reactivities[19] owing to the stronger -$CH_2$–I bond, the cross-IDT of 1,2- and 2,1-units [Eq. (7b)] is shifted towards irreversible accumulation of unreactive $P_n$-$CF_2$-$CH_2$-I (Figure S7), the IDT of which [Eq. (7c)] is kinetically irrelevant[19] and contributes to polydispersity index (PDI) broadening. The IDT-CRP[15,16,19–21] (Figure 1; Figure S8; Table S5) was demonstrated by the linear dependence of $M_n$ on conversion and reasonable PDI values (approximately 1.5). As expected, almost identical $M_n$ profiles were obtained at constant [VDF]/[I$(CF_2)_6$I] ratios, regardless of the HVIC type or amount (Figure S8a), and the $M_n$ scaled only with the [VDF]/[I$(CF_2)_6$I] ratio (Figure 1). The more efficient[24–28,40,43] IFAB provided seven times faster polymerizations than IDAB and DMPI (Figure S8b). The head-to-head defects were intercepted as $P_m$-$CF_2$-$CH_2$-I[19] and strongly suppressed (Figure S5a,b). While the concentration of $P_m$-$CF_2$-$CH_2$-I increases and that of $P_m$-$CH_2$-$CF_2$-I decreases with conversion,[19] their sum, the total iodine chain end functionality, remains reasonable (> 90 %, Figure S7) for block copolymer synthesis.[19]

While the above method affords VDF-CRP, the amount of trifluoromethylation is minimal. However, if instead of I$(CF_2)_6$I, $CF_3$I were the chain transfer agent, all chains would be trifluoromethylated. Moreover, as $I_2$ does not initiate VDF,[19,21] but traps radicals at diffusion-controlled rates,[47] we wondered if HVIC/$I_2$ could be used for in situ $CX_3$I and PVDF-I[48] generation towards IDT (Scheme 1).

Indeed, $CX_3$ initiations thus became available (Figure S9). However, only free radical polymerizations (Figure S10) and no iodine chain ends (Figure S9a) resulted for IDAB and DMPI, while IFAB afforded IDT-CRP (Figure 2), PVDF-I, (Figure S9) and a three times faster polymerization without an induction time (Figure S10). This indicates that all $I_2$ was rapidly depleted in a fast HVIC[24–32,42] reaction [Eqs. (5) and (5′)], where the resulting $CX_3$COOI was subsequently consumed by photo-[27–32,44] and $CX_3^{\bullet}$ induced decarboxylation to $CX_3$I [Eqs. (4d) and (6)]. Therefore, $CX_3$I formed faster[44] and accumulated before $CX_3^{\bullet}$ slowly[38] photoreleased from the remaining HVIC, begun initiating VDF. Qualitatively, this is consistent with the reaction color sequence (Figure S2), where the initial violet $I_2$ quickly (less than five minutes) dissipates into the dark-orange $CX_3$COOI,[42] which fades (1–2 hours) to a colorless solution and finally, to a white polymer.

Since all $I_2$ serves only to generate $CX_3$I before PVDF$^{\bullet}$ forms, polymerizations where [VDF]/[$I_2$]/[HVIC] = $a/b/c$ are equivalent with [VDF]/[$CX_3$I]/[HVIC] = $a/2b/(c-b)$ (IDAB, IFAB) or $a/2b/(1.5c-b)$ (DMPI). Understandably, as IDAB and DMPI provide $CH_3$I (not capable of IDT),[15,16,19–21] they also only afford free radical polymerizations. By contrast, IFAB promotes IDT just like VDF/$R_F$I/HVIC ($R_F$I = $CF_3$I).[15,16,19–21] However, because IFAB is now both the initiator and CTA precursor, all initiator chain ends are trifluoromethylated (Figure S9).

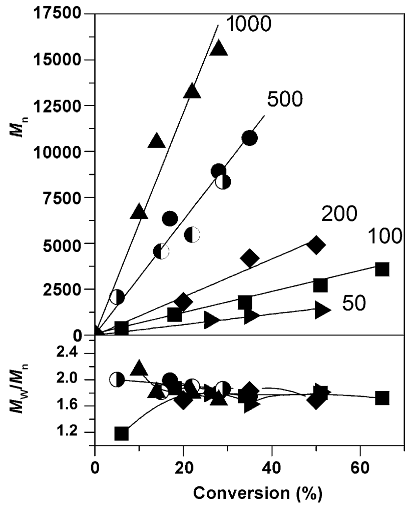


***Figure 2.*** Dependence of $M_n$ and $M_w/M_n$ on conversion in VDF polymerizations initiated from IFAB in the presence of $I_2$: [VDF]/[$CF_3$I]/[IFAB] (where [VDF]/[$I_2$]/[IFAB]) = 50/1/0.5 (▶, 50/0.5/1), 100/1/1.5 (■, 50/0.25/1), 200/1/1.5 (◆, 100/0.25/1), 500/1/0.5 (◐, 250/0.25/0.5), 500/1/1 (◑, 250/0.25/0.75), 500/1/1.5 (●, 250/0.25/1), and 1000/1/1.5 (▲, 500/0.25/1).

IDT-CRP was demonstrated again by the linear dependence of $M_n$ on conversion (Figure 2; Figure S11). The proposed $I_2 \Leftrightarrow 2\,CF_3I$ equivalence and the IDT mechanism are supported, irrespective of IFAB ratio, by the same $M_n$ profile at constant [VDF]/[$I_2$] levels, by the scaling of $M_n$ only with [VDF]/[$I_2$] ratio, and by the similar $M_n$ profiles (Figure S12) in comparisons that satisfy the [VDF]/[$CF_3$I]/[IFAB] = [VDF]/[I$(CF_2)_6$I, $CF_3(CF_2)_3$-I]/[IFAB, IDAB, DMPI] equation.

Finally, the synthesis of complex, $CF_3$ containing macromolecules was demonstrated with novel block copolymers of VDF with 2,2,2-trifluoroethyl methacrylate and methyl-2-(trifluoromethyl)acrylate, using $Mn_2(CO)_{10}$ for the activation[19] of $CF_3$-PVDF-I (Figure S13).

To summarize, by contrast to their classic use as oxidants, the metal-free, visible-light, radical photodecarboxylation of HVICs enables their use as stable and convenient synthetic equivalents of their inaccessible peroxide or azo analogues, while the inexpensive $CX_3COOH$ feed stock qualifies IFAB, IDAB, and DMPI as the least expensive and most convenient $CX_3^\bullet$ and $CX_3I$ precursors for radical (trifluoro)(iodo)methylations. The practicality of HVICs was illustrated by their role as $CX_3^\bullet$ photoinitiators and $CX_3I$ CTAs for metal-free, green VDF CRPs performed in glass tubes under very mild conditions, with external ($I(CF_2)_6I$) or in situ generated ($CF_3I$) CTAs, through the first instance of $I_2$-VDF-IDT. Finally, the PVDF iodine chain ends were exploited in the synthesis of well-defined block copolymers.

These concepts are equally applicable to the radical trifluoromethylation of other alkenes or arenes and to the IDT-CRP of other monomers. The use of a wide set of RCOOH precursors enables the generation of libraries of radical initiators and iodine CTAs with applications in both organic chemistry and the photomediated synthesis of architecturally complex fluoromaterials.

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